

Final Report

**Central California Ozone Study
Volatile Organic Compounds Collection and Analysis
by the Canister and Tenax Methods**

Prepared for

San Joaquin Valley Air Pollution Study Agency

c/o

State of California Air Resources Board

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1. INTRODUCTION

The Central California Ozone Study (CCOS) is a multi-year program of meteorological and air quality monitoring, emission inventory development, data analysis, and air quality simulation modeling. Among the goals of this study was the execution of a large-scale field study in summer 2000 to acquire a comprehensive database to support modeling and data analysis (Fujita et al., 2000). Air samples were collected in parts of central and northern California. This study area reflects the regional nature of the state 1-hour and federal 8-hour ozone exceedances and increasing urbanization of traditionally rural areas. CCOS is funded by the San Joaquin Valley-wide Air Pollution Study Agency, a joint powers agency (JPA) formed by the nine counties in the Valley. On a day-to-day basis, the California Air Resources Board is responsible for management of the study.

The CCOS field measurement program was conducted during a four-month period from 6/1/00 to 9/30/00. Additional data were collected during ozone episodes (intensive operational periods (IOPs)) to better understand the dynamics and chemistry of the formation of high ozone concentrations. These episodes occurred on July 23-24 (IOP 1), July 30-August 1 (IOP 2), August 14 (IOP 3) and September 17-21, 2000 (IOP 4). The data collected using canisters and Tenax during the IOPs are presented here.

The collection sites that were analyzed by the Organic Analytical Laboratory (OAL) are listed in Table 1-1. Figure 1-1 shows the locations of existing monitoring stations measuring carbon monoxide and speciated hydrocarbons and carbonyl compounds in relation to the CCOS supplemental monitoring sites.

Table 1-1. CCOS Supplemental Surface Air Quality Monitoring Sites and Measurements in the Sacramento Valley and Northern Sierra Nevada Foothills.

Site	County	Site Code	Type	Continuous Analyzers	VOC Sampling	VOC Analysis
San Leandro	Alameda	SLE	S1	BAAQMD	BAAQMD	DRI, AtmAA
Sutter Buttes	Sutter	SUT	S1	ARB	DRI	DRI, AtmAA
White Cloud	Nevada	WHC	S1		DRI	DRI, AtmAA
Bethel Island	Contra Costa	BTI	S2	BAAQMD	BAAQMD	DRI, AtmAA
Patterson Pass	Alameda	PAP	S2	UCB	UCB	DRI, AtmAA
Trimmer	Fresno	TRM	S2	ARB	ARB	DRI, AtmAA
Granite Bay	Placer	GRB	R	DRI	DRI	DRI, AtmAA
Parlier	Fresno	PLR	R	SJVUAPCD	SJVUAPCD	DRI, AtmAA, ARB
Sunol	Alameda	SUN	R	UCB	DRI	DRI, AtmAA

ATMAA performed the analysis of the DNPH cartridges for carbonyl compounds.

Type 1 supplemental monitoring sites (S1) are intended to establish boundary and initial conditions for input into air quality models. These sites are located at the upwind boundaries of the modeling domain, in the urban center (initial conditions) and at downwind locations (boundary conditions).

Type 2 supplemental monitoring sites (S2) are located at the interbasin transport and intrabasin gradient sites, and near the downwind edge of the urban center where ozone formation may either be VOC or NO_x limited depending upon time of day and pattern of

pollutant transport. S2 sites also provide data for initial conditions and operation evaluations and some diagnostic evaluation of model outputs.

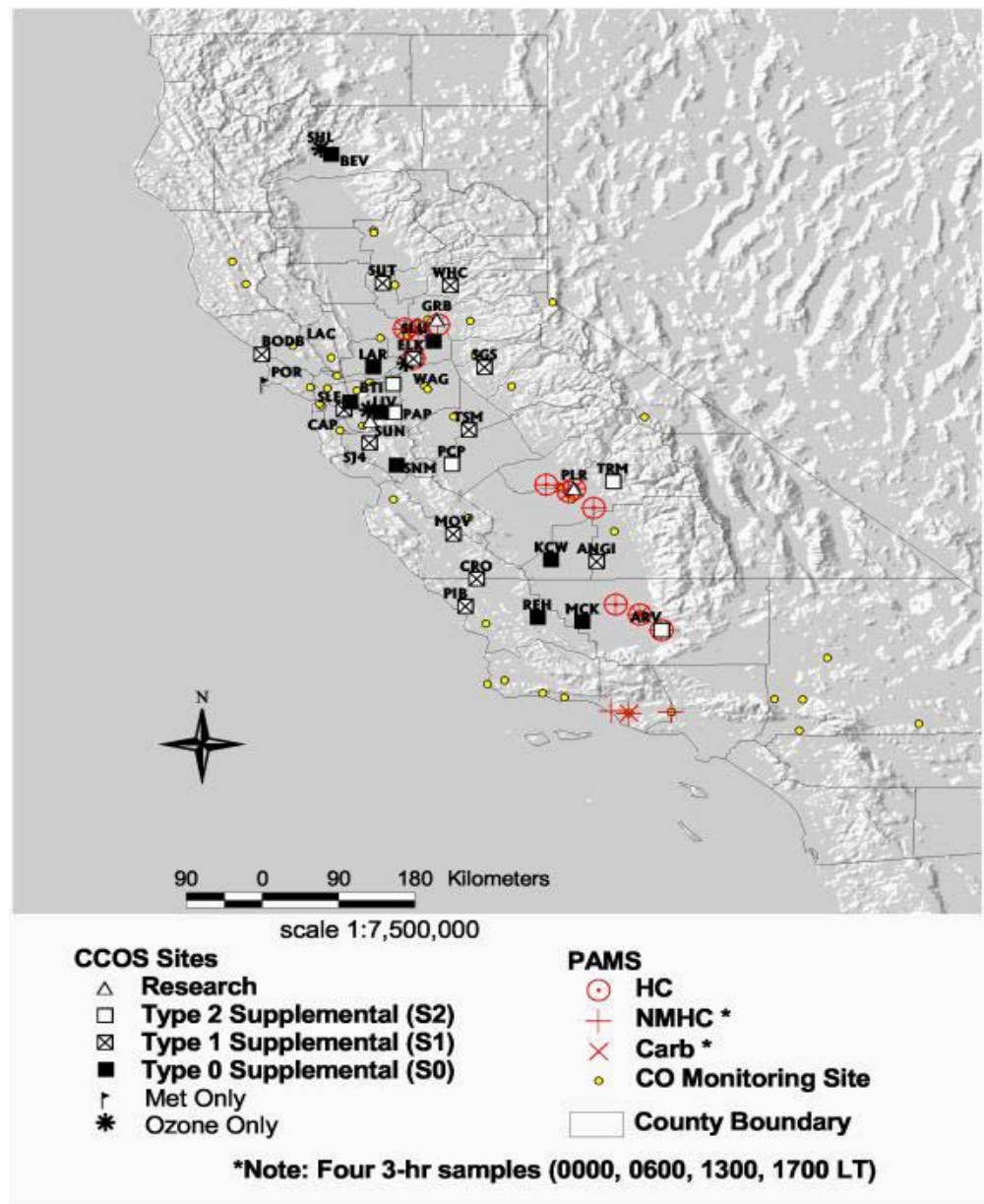


Figure 1-1. CCOS supplemental air quality and meteorological monitoring sites and Photochemical Assessment Monitoring Stations.

Research sites (R) have the same site requirements as S2 sites. The sites are intended to measure a representative urban mix of pollutants, and were carefully selected to minimize the potential influence of local emission sources. As with S2 sites, research sites are located where ozone formation may either be VOC or NO_x limited depending upon time of day and pattern of pollutant transport. These sites possessed a broader range of modern equipment than the other sites, such as a continuous GC/MS and Tenax samplers.

1.1 Intensive Operational Periods

Four Intensive Operational Periods (IOPs) were performed during the summer of 2000: July 23-24 (IOP 1), July 30-August 1 (IOP 2), August 14 (IOP 3) and September 17-21, 2000 (IOP 4). Four canister samples were collected each day of the IOPs at each site (S1, S2 and R) as three-hour integrated samples: 0000 hours – 0300 hours, 0600 hours – 0900 hours, 1300 – 1600 hours, and 1700 hours – 2000 hours (PDT). Tenax samples were collected on the same time schedule at the Research sites only.

2. EXPERIMENTAL

2.1 Canister Samples

Prior to collection, electropolished canisters were cleaned by alternating evacuation and flushing with humid ultra high purity air at 140 °C through seven cycles. Ten percent of the cleaned canisters were then pressurized with humid ultra high purity air, allowed to equilibrate over night, then analyzed by gas chromatography with flame ionization detection (GC/FID). For a blank value, the total non-methane hydrocarbon concentration was approximately 5 ppbC, well within acceptable values.

Each whole air sample was collected for three hours by pressurized sampling at a flow rate of 40 cc/min to 20-25 psi in stainless steel canisters, and was analyzed by gas chromatography with flame ionization detection (GC/FID), as described elsewhere (Zielinska et al., 1996). A 60 m x 0.32 mm DB-1 capillary column (J & W Scientific, Inc.) was employed to separate the VOCs from C₂-C₁₂ with a temperature program starting at –65 °C for 2 minutes followed by an increase in temperature of 6 °C/minute to 223 °C. A 30 m x 0.53 mm ID PLOT column was used to separate the light VOCs (C₂-C₅) with a temperature program starting at 50 °C for 1 minute followed by an increase in temperature of 12 °C/minute to 200 °C. Helium (Sierra Airgas, UHP) was used as the carrier gas. The GC-FID response was calibrated in ppbC using National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) 1805 (254 ppb benzene in nitrogen) for the C₂-C₁₂ compounds and SRM 2764 (735 ppbC propane in air) for the C₂-C₅ compounds.

2.2 Tenax Samples

Prior to use, the Tenax-TA solid adsorbent was cleaned by Soxhlet extraction with hexane/acetone mixture (4/1 v/v) overnight, and dried in a vacuum oven at ~80 °C. The dry Tenax was packed into Pyrex glass tubes (4 mm i.d. x 15 cm long, each tube containing 0.2 g of Tenax) and thermally conditioned for four hours by heating in an oven at 300 °C under a nitrogen purge (25 ml/min nitrogen flow). Approximately 10% of the precleaned Tenax cartridges are tested by GC/MS for quality assurance prior to sampling. After cleaning, the Tenax cartridges were capped tightly using clean Swagelok caps (brass) with graphite/vespel ferrules, placed in metal containers with activated charcoal on the bottom, and kept in a clean environment at room temperature until use.

The Tenax samples were analyzed by thermal desorption-cryogenic pre-concentration, using the Chrompack CP4020 Thermal Desorption Cold Trap Injector unit with the Stand Alone CP4010/4020 Controller (Chrompack International BV), followed by high resolution gas chromatography and Fourier transform infrared detection (IRD) – mass spectrometry detection (MSD) (Hewlett Packard 5890II GC, 5965 IRD and 5970 MSD) (see Figure 2.2-1). Samples were desorbed at 300 °C for 14 minutes, cryogenically pre-concentrated at –150 °C

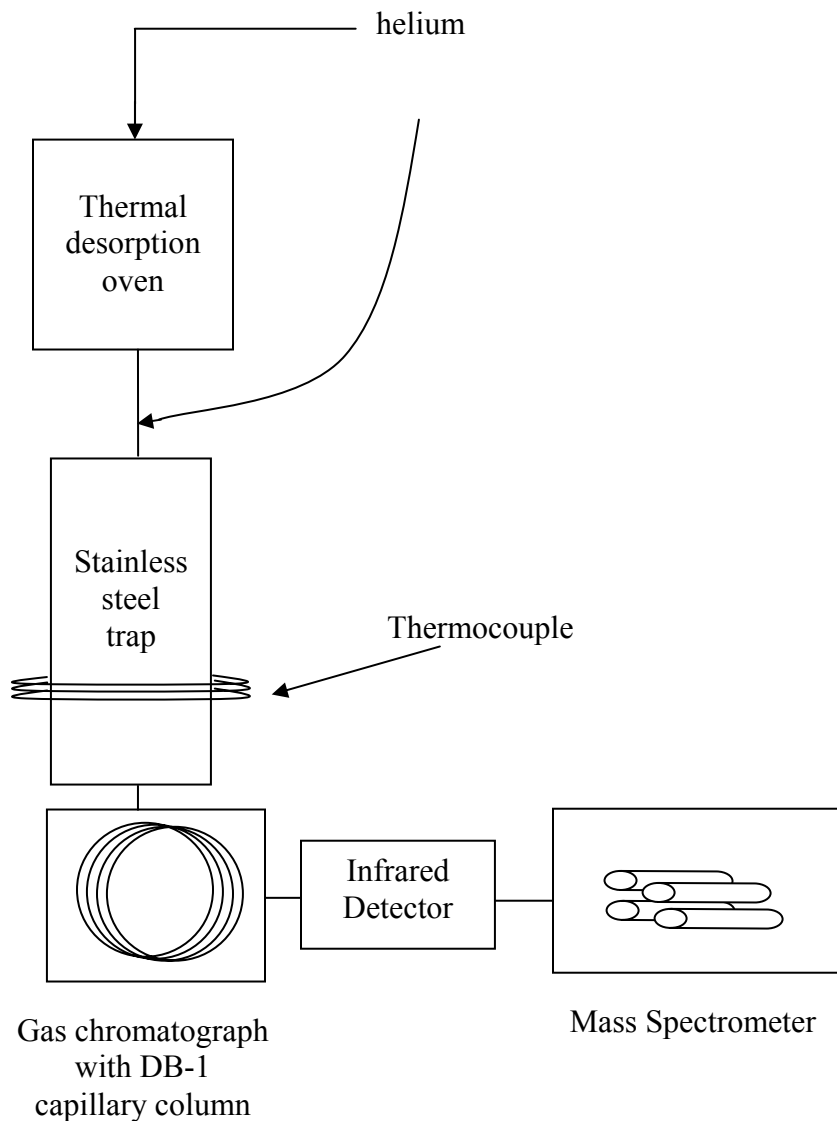


Figure 2.2-1. Diagram of Hewlett Packard 5890II GC, 5965 IRD and 5970 MSD

on 30 cm deactivated silica capillary tubing (0.52 mm i.d.) packed with a small amount of glass wool, followed by secondary desorption at 280 °C for 1 minute. Separation of the target VOCs was achieved using a 60 m x 0.32 mm DB-1 capillary column (J & W Scientific, Inc.). The temperature program consisted of 30 °C for 2 minutes, followed by a temperature increase of 6 °C/min to 280 °C, and finally 280 °C was held for 10 minutes. Before analysis, each sample was spiked with 1 ml of an internal standard, 1-fluoronaphthalene, then flushed with ultra high purity helium for 2 minutes. Compounds were quantified using the mass spectrometer. A standard mixture was analyzed each day to account for any detector drift.

2.3 Calibration

2.3.1 Canisters

The GC/FID response is calibrated in ppbC using primary calibration standards traceable to the National Institute of Standards and Technology (NIST) Standard Reference Materials (SRM). The NIST SRM 1805 (254 ppb of benzene in nitrogen) was used for calibrating the analytical system for C2-C12 hydrocarbon analysis. The 1 ppm propane in nitrogen standard

(Scott Specialty Gases, periodically traced to SRM 1805) was used to calibrate the light hydrocarbon analytical system. Based on the uniform carbon response of the FID to hydrocarbons, the response factors determined from these calibration standards were used to convert area counts into concentration units (ppbC) for every peak in the chromatogram.

Identification of individual compounds in air samples were based on the comparison of linear retention indices (RI) with RI values of authentic standard compounds and RI values obtained by other laboratories performing the same type of analysis using the same chromatographic conditions (Auto/Oil Program, Atmospheric Research and Exposure Assessment Laboratory, EPA). The DRI laboratory calibration table contains 160 species. Three to five concentration levels of the standard with two to three injections per calibration level were used to generate calibration curves (U.S. EPA).

2.3.2 Tenax

For calibration of the GC/MS standard, Tenax cartridges are prepared by spiking cartridges with a methanol solution of standard hydrocarbons, prepared from high-purity commercially available C8-C20 aliphatic, oxygenated and aromatic hydrocarbons. The solvent is then removed with a stream of N₂ (2 min, 100 ml/min at room temperature) and the Tenax cartridges are thermally desorbed into the GC system, as described above. Three concentrations of each standard compound are employed. Two to three repeated sample injections per calibration level are made. Area response factors per nanogram of compound per Tenax cartridge are calculated for each concentration. All response factors are recorded in the ChemStation software program and the mean or median value taken. It has also been verified that the variations in the response factors for individual hydrocarbons in the C8-C20 range do not exceed ~10 % with the exception of the straight chain alkanes, for which daily calibrations are recorded.

3. RESULTS

3.1 Canisters

The results of the analyses conducted by the Organic Analytical Laboratory for all canister and Tenax samples were submitted electronically to CARB. The data for selected hydrocarbons at three research sites for IOP 4 are presented in Tables 3.1-1 and 3.1-2. Table 3.1-1 shows the concentrations (ppbC) of selected hydrocarbons and the total nonmethane hydrocarbons for the three research sites. The concentrations of these compounds are presented in order to show the importance of photochemistry downwind of urban areas. Figures 3.1-1 through 3.1-3 illustrate the data shown in Table 3.1-1, and demonstrate graphically the anti-correlation of isoprene with the other selected hydrocarbons. Higher concentrations of isoprene in the afternoon samples are an indication of biogenic sources, as vegetation emissions of isoprene increase with increasing temperature and light intensity.

Table 3.1-1. Concentrations (ppbC) of selected hydrocarbons for three research sites.

day	time	propene	acetylene	isoprene	benzene	toluene	mp-xylene	Tot NMHC
Parlier								
9/18/2000	600-900	3.51	7.3	0.54	3.62	11.8	7.33	223.75
9/18/2000	1300-1600	0.3	3.04	0.34	1.13	2.7	0.92	70.71
9/19/2000	1300-1600	0.13	1.79	0.15	0.99	1.65	0.39	62.01
Granite Bay								
9/17/2000	600-900	0.87	1.16	2.74	0.68	3.79	1.11	47.12
9/17/2000	1300-1600	0.28	0.91	4.36	0.58	1.53	0.64	34.32
9/18/2000	600-900	1.31	1.97	2.25	1.12	5.35	2.7	70.29
9/18/2000	1300-1600	0.5	2.99	4.78	1.37	4.75	1.83	66.23
Sunol								
9/17/2000	600-900	6.8	8.01	0.84	3.62	11.14	5.99	146.85
9/17/2000	1300-1600	0.33	0.64	6.09	0.7	0.87	0.42	29.72
9/18/2000	600-900	5.85	3.16	1.3	2.05	4.86	3.18	81.28
9/18/2000	1300-1600	2.99	4.71	3.88	2.36	6.53	3.12	95.55

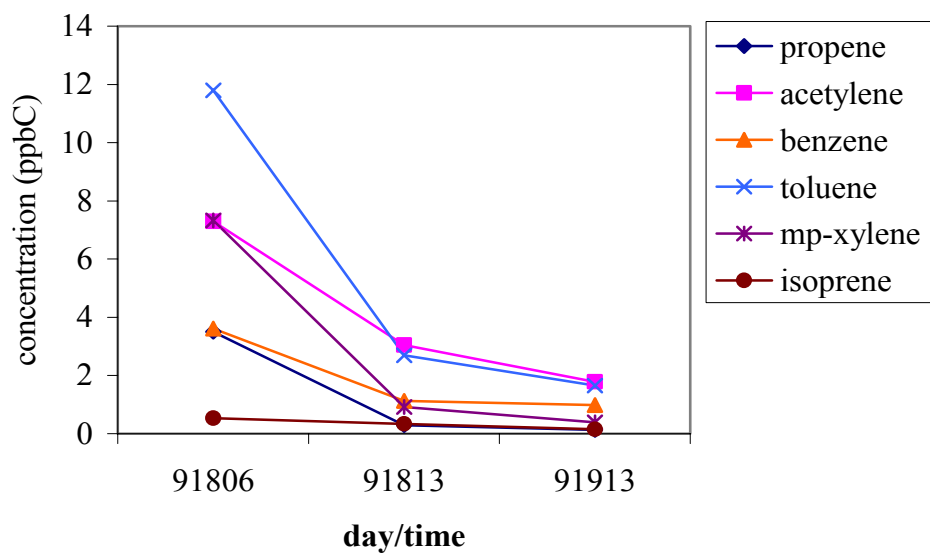


Figure 3.1-1. Parlier during episode 4.

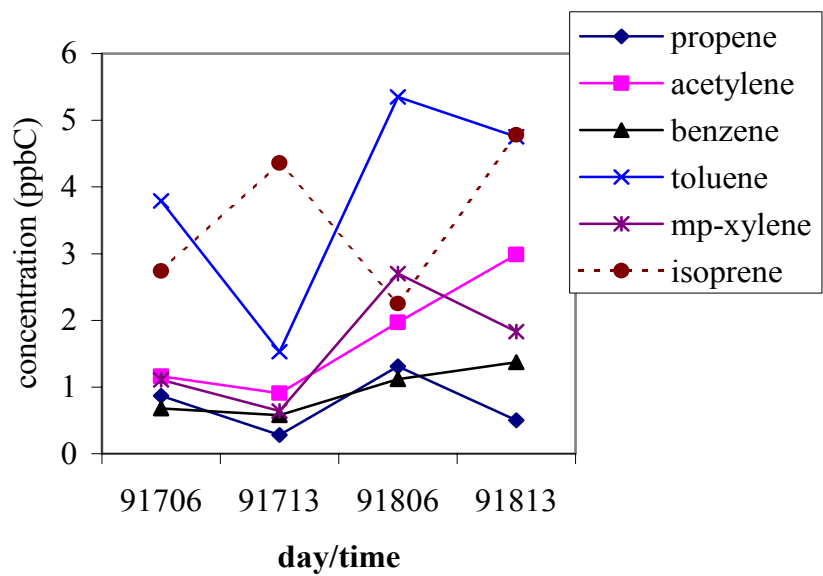


Figure 3.1-2. Granite Bay during episode 4.

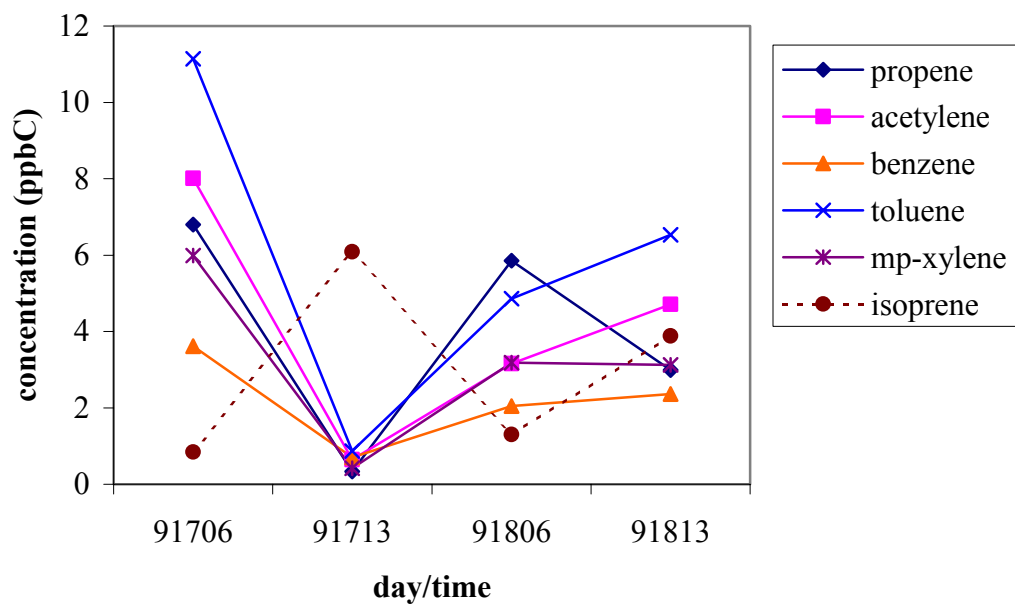


Figure 3.1-3. Sunol during episode 4.

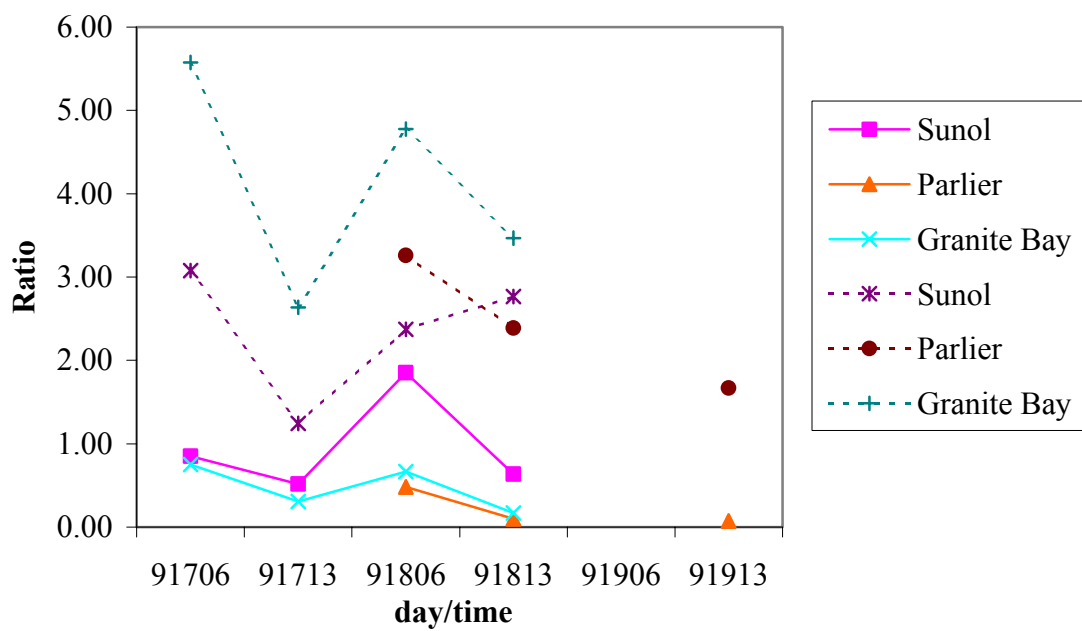


Figure 3.1-4. Ratios of propene/acetylene (solid lines) and toluene/benzene (dashed lines) for the three research sites during episode 4.

Table 3.1-2 shows the ratios of propene to acetylene, toluene to benzene and total xylenes to benzene for these same samples. The diurnal patterns shown for the ratios of propene to benzene and toluene to benzene in Figures 3.1-4 and 3.1-5 indicate photochemistry plays a role in the removal of these compounds, due to the high reactivity of propene, toluene and xylenes relative to acetylene and benzene, in addition to meteorological transport. (In each of the figures, the x-axis labels refer to the sample in the following manner: the first number indicates the month, followed by the day and time.) This diurnal pattern may also be seen in Figures 3.1-5 and 3.1-6, which shows the ratio of propene to acetylene and toluene to benzene at the six supplemental sites. A unique feature in Figure 3.1-6 is the spike in the toluene to benzene ratio at the White Cloud site on September 19 from 1700-2000 hours, and again on September 21 from 0600 to 0900 hours. This is likely due to a local source releasing a burst of toluene.

Table 3.1-2. Ratios of propene to acetylene and toluene to benzene for three research sites.

site	day	time	propene/acetylene	toluene/benzene	Total xylene/benzene
Parlier	9/18/2000	600-900	0.48	3.26	2.78
	9/18/2000	1300-1600	0.10	2.39	1.19
	9/19/2000	1300-1600	0.07	1.67	0.61
Granite Bay	9/17/2000	600-900	0.75	5.57	2.21
	9/17/2000	1300-1600	0.31	2.64	1.57
	9/18/2000	600-900	0.66	4.78	3.33
	9/18/2000	1300-1600	0.17	3.47	1.93
Sunol	9/17/2000	600-900	0.85	3.08	2.31
	9/17/2000	1300-1600	0.52	1.24	0.86
	9/18/2000	600-900	1.85	2.37	2.12
	9/18/2000	1300-1600	0.63	2.77	1.86

As discussed by Roberts (Roberts et al., 1998), a high xylenes to benzene ratio (>2) indicates fresh emissions of xylenes. In the case of all three research sites, the total xylenes to benzene ratios are consistently above 2 in the morning samples, showing the car exhaust emissions during the morning commute has the biggest impact on the concentrations of the xylenes. The lower ratios in the afternoon samples indicate the importance of photochemistry.

Parrish (Parish et al., 1998) suggests using the concentration ratio of isobutane to n-butane to provide a quantitative test for internal consistency. Although they are emitted from a variety of sources, these compounds have similar reactivity and are mixed rapidly relative to their photochemical lifetimes. Parrish states the mean ratio of the butane isomers should be in the range of 0.4. to 0.6. In this study, the calculated mean ratio is 0.55 ± 0.04 , well within the stated requirements. Figure 3.1-7 illustrates the correlation of isobutane and butane, with an $r^2 = 0.83$.

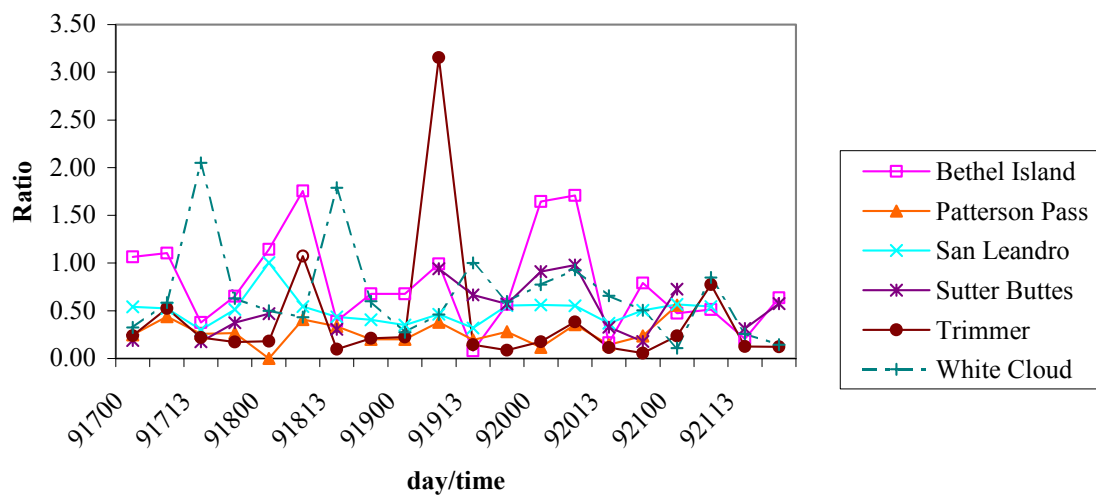


Figure 3.1-5. Ratio of propylene/acetylene for the supplemental sites.

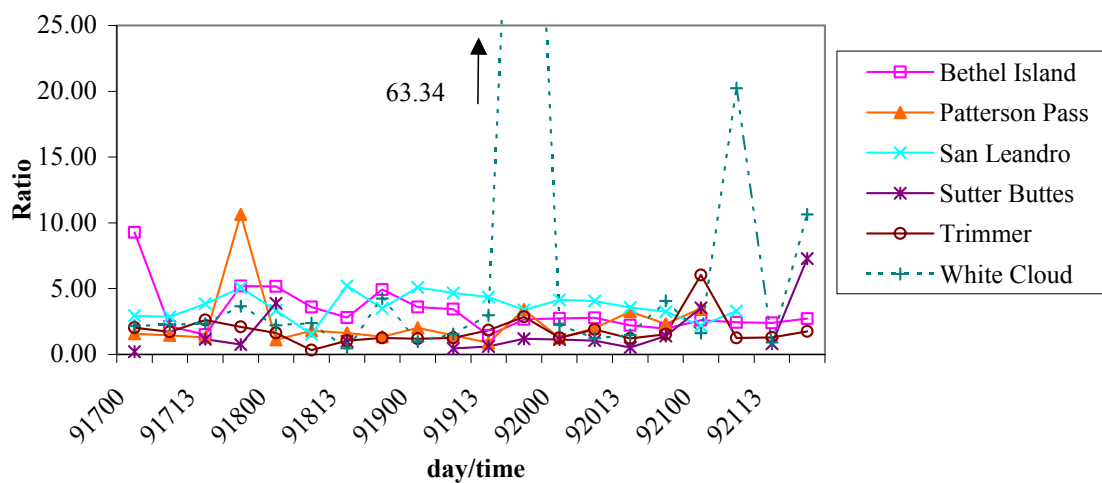


Figure 3.1-6. Ratios of toluene/benzene at the supplemental sites.

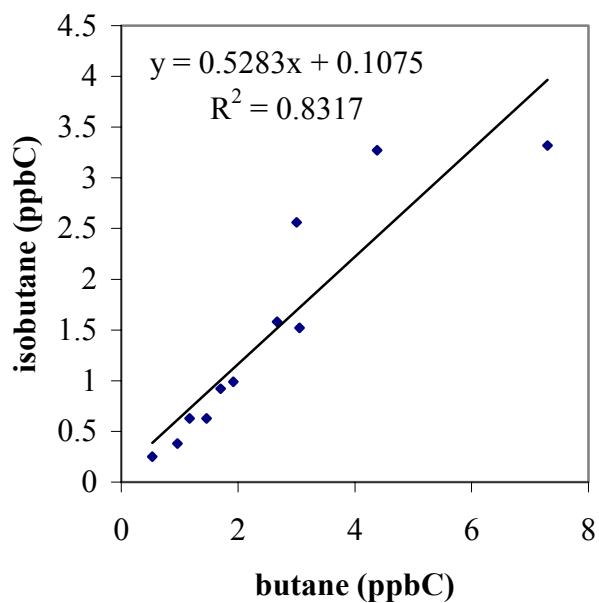


Figure 3.1-7. Correlation plot for butane isomers.

Figures 3.1-8 and 3.1-9 show the correlation of benzene to acetylene and ethyl benzene to toluene, respectively. Benzene and acetylene show an $r^2 = 0.96$, and are expected to correlate well, as they have common sources. Ethyl benzene and toluene do not correlate well in the data presented here, which may be an indication that these compounds were emitted from different sources ($r^2 = 0.2688$).

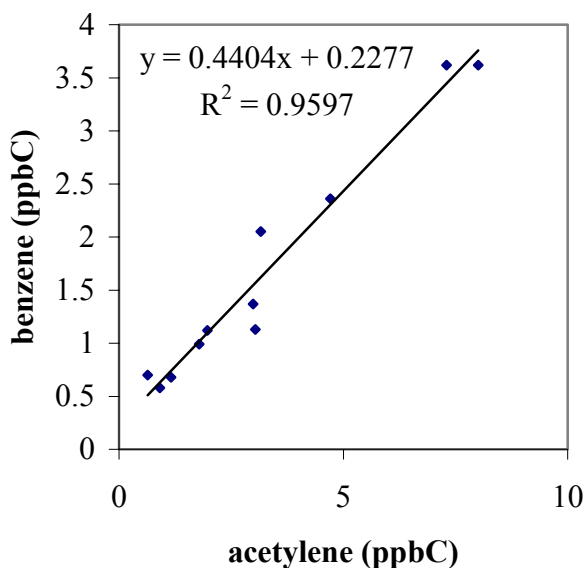


Figure 3.1-8. Correlation plot for benzene and acetylene.

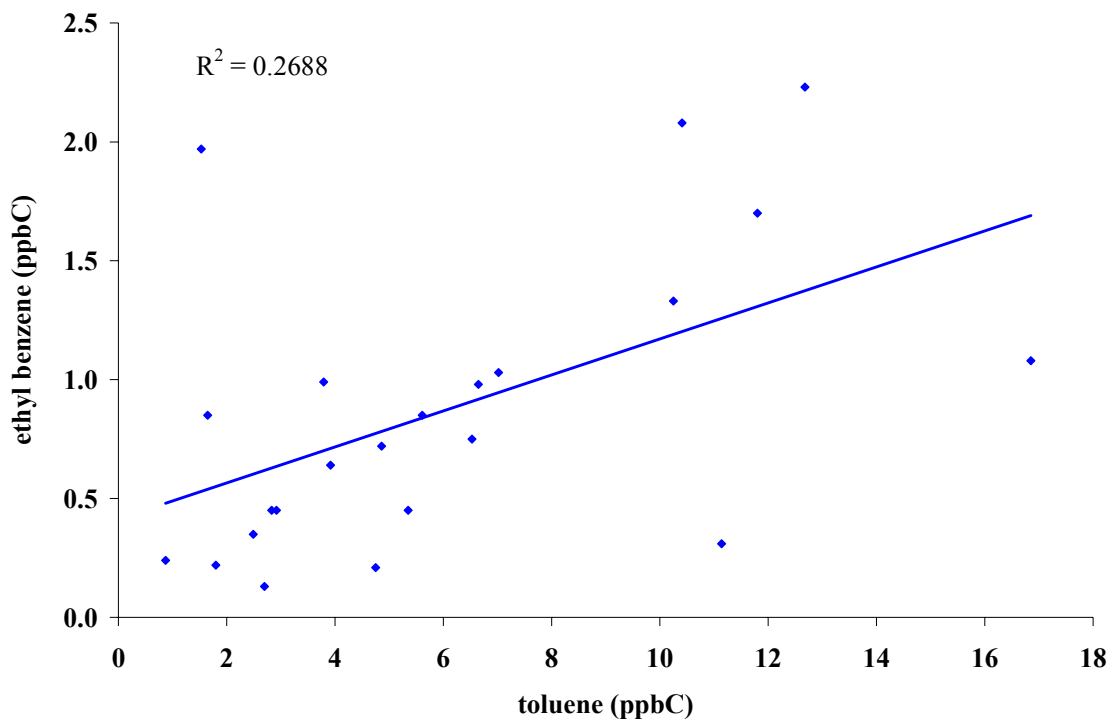


Figure 3.1-9. Correlation plot for toluene and ethyl benzene.

3.2 Comparison of Canisters and Tenax

Tenax samples were collected at each research site during each IOP, while canister samples were only collected during IOPs 1, 2 and 4. Figure 3.2-1 illustrates a comparison of ethyl benzene concentrations between Tenax and canister samples for the three episodes in which canisters samples were collected. Two Tenax samples shown in this figure do not follow the trend indicated by the remaining samples. This may be caused by inaccurate measurements of flow rates through the Tenax tubes at the time of sampling. Excluding these two points, the correlation between the Tenax samples and canister samples is $r^2 = 0.73$, an improvement over the original r^2 of 0.1353. However, the slope of the line is 0.5, well below a correspondence of 1:1. This may indicate break through for ethyl benzene in Tenax samples at the volumes collected in this study. Figures 3.2-2 and 3.2-3 show similar comparisons for m,p-xylene and o-xylene, respectively. For these compounds, correlation is high $r^2 = 0.80$ and $r^2 = 0.79$, but again the slope of the line is approximately 0.5, indicating possible break through problems for these compounds.

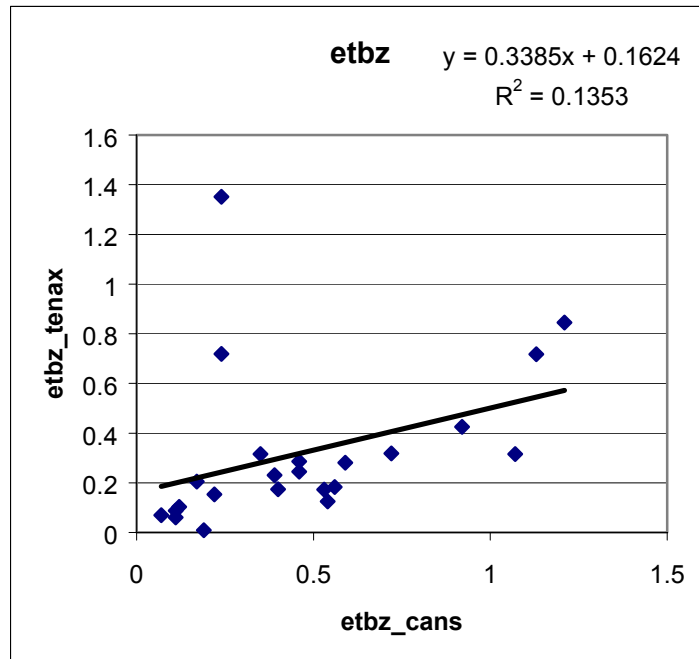


Figure 3.2-1. A correlation plot for ethyl benzene for canisters and Tenax.

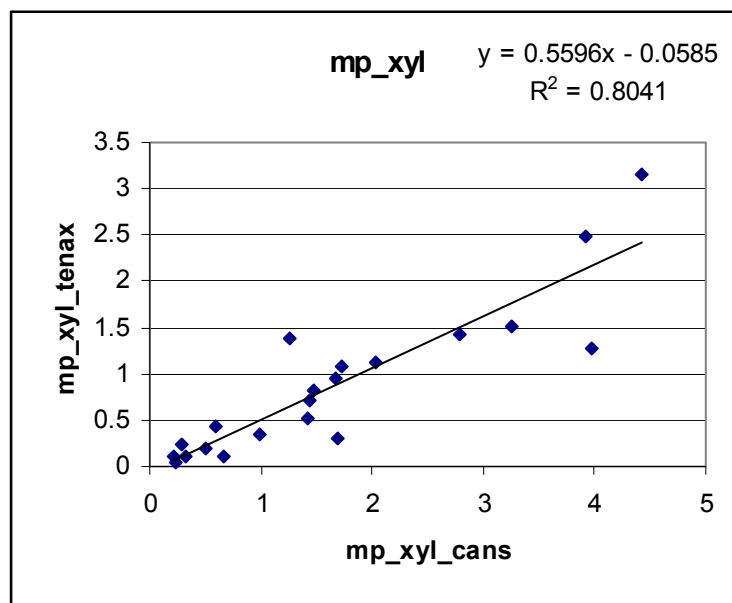


Figure 3.2-2. A correlation plot for m,p-xylene for canisters and Tenax.

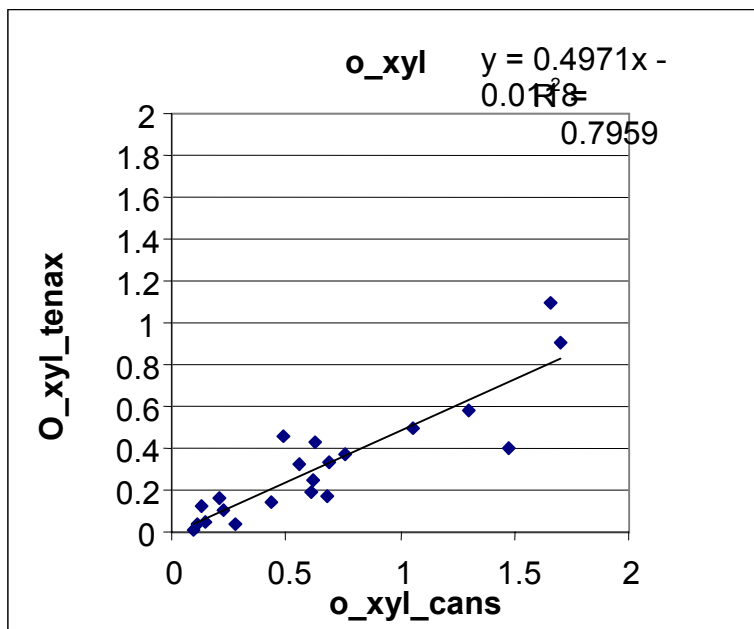
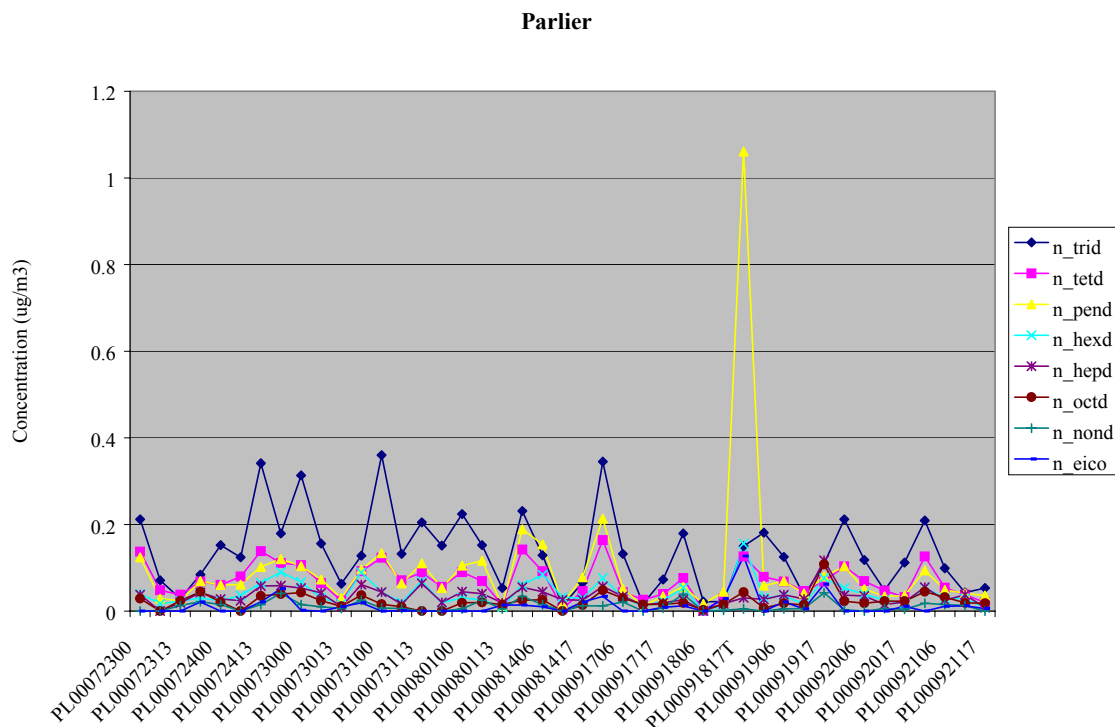
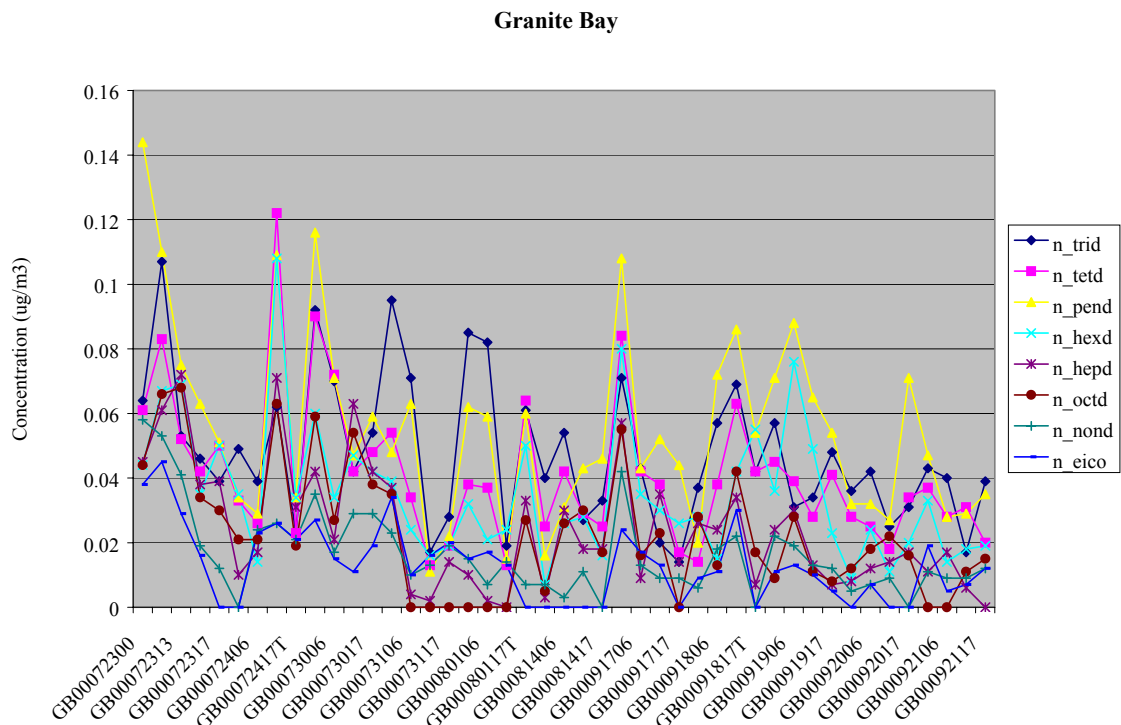


Figure 3.2-3. A correlation plot for o-xylene for canisters and Tenax.

3.3 Tenax

The C13 to C20 straight chain alkanes are quantified for the Tenax samples, and are compounds unique to this sampling media in this study. Figures 3.3-1 through 3.3-3 show n-tridecane through eicosane measured for each IOP at the three research sites: Granite Bay, Parlier and Sunol. These compounds follow a diurnal pattern with values peaking in the late afternoon.



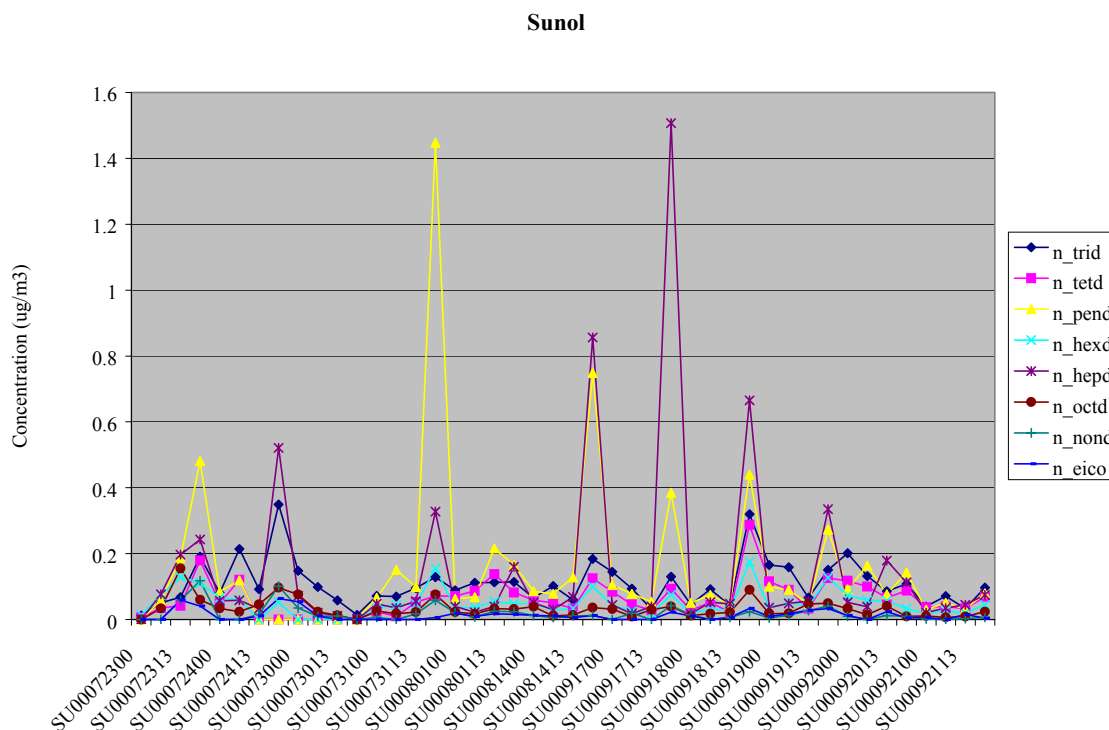


Figure 3.3-3. Tenax samples collected at Sunol, California.

4. CONCLUSIONS

The work conducted by the Organic Analytical Laboratory at the Desert Research Institute for the Central California Ozone Study involved collecting and analyzing samples collected at sites around central California using canisters for CO, CO₂, methane, and C₂-C₁₂ hydrocarbons for six supplemental sites and three research sites, and Tenax for VOCs ranging from C₈ to C₂₀. The ratios of propene to acetylene and toluene and xylenes to benzene are indicators of removal by chemistry, as propene is more reactive than acetylene, and toluene and xylenes more than benzene. Benzene and acetylene showed excellent correlation, while ethyl benzene and toluene did not, which may be an indication that they were emitted from different sources. When canister and Tenax samples were compared for the compounds ethyl benzene and the xylenes, two samples were revealed to possess sampling errors that may have been caused by inaccurate measurements of flow rates through the Tenax tubes. Also, these compounds showed high correlation but did not show a 1:1 correspondence, possibly indicating break through problems for these compounds.

5. REFERENCES

Fujita, E., Keislar, R., Stockwell, W., et al. (2000). Central California Ozone Study (CCOS) Volume II: Field Operations Plan, Desert Research Institute, Reno, NV.

Parrish, D.D., Trainer, M., Young, V., Goldan, P.D., Kuster, W.C., Jobson, B.T., Fehsenfeld, F.C., Lonneman, W.A., Zika, R.D., Farmer, C.T., Riemer, D.D., and M.O. Rodgers (1998), Internal Consistency Tests for Evaluation of Measurements of Anthropogenic Hydrocarbons in the Troposphere. *J. Geophys. Res.*, **103**, 22339-22359.

Roberts, P.T., MacDonald, C.P., Main, H.H., Dye, T.S., Coe, D.L., and T.L. Haste (1997). Analysis of Meteorological and Air Quality Data for the 1996 Paso del Norte Ozone Study. STI-997330-1754-FR, Sonoma Technology Inc., Santa Rosa, CA.

Zielinska, B., Sagebiel, J., Harshfield, G., Gertler, A.W., and W.R. Pierson (1996). Volatile Organic Compounds in the C₂–C₂₀ Range Emitted from Motor Vehicles: Measurement Methods. *Atmos. Environ.*, **30**, 2269-2286.